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APPLICATION OF IMPREGNATED  
DISPENSER-TYPE INSERTS  
IN HOLLOW CATHODES**

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MATERIALS: Interaction with Sea-Level  
Ambient Atmospheres and Decomposition  
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## TECHNOLOGY DEVELOPMENT FOR APPLICATION OF IMPREGNATED DISPENSER-TYPE INSERTS IN HOLLOW CATHODES

### BARIUM CALCIUM ALUMINATE IMPREGNANT MATERIALS: Interaction with Sea-Level Ambient Atmospheres and Decomposition Behaviors of Reaction Products

#### Abstract

It has long been recognized that aluminate-type impregnant materials, as used in dispenser cathodes, react with certain constituents of the sea level ambient atmosphere. Several potentially damaging consequences of such reactions have been noted. One is "blooming", or the appearance of small amounts of impregnant-derived reaction products on the cathode surface, typically at pore ends, resulting in a hazy appearance, and which, in the extreme, as a result of significant volume expansion may crack the surrounding cathode matrix. A second issue is the possibility of detrimental chemical reactions involving the evolving decomposition products which can occur during heating of the cathode subsequent to exposure.

The details of the chemistry involved have not been the subject of comprehensive investigation, and the historical level of knowledge has been largely empirically derived. It is widely believed that hydrolysis of the barium calcium aluminate (BCA) impregnant as a result of exposure to atmospheric water vapor is the critical chemical process.

Studies to systematically determine the effects of exposure of the commonly used  $4\text{BaO} \cdot 1\text{CaO} \cdot 1\text{Al}_2\text{O}_3$  composition (4:1:1) have been undertaken. In addition the decomposition behavior of the reaction products has been characterized.

A number of analytical tools, including thermogravimetric analysis (TGA), differential thermal analysis (DTA) and x-ray diffraction (XRD) have been applied to characterize the reactions occurring between the impregnant material and sea level ambient atmosphere and during heating of the impregnant material after atmospheric exposure.

Substantial weight losses, over the temperature range from room temperature to  $1050^\circ\text{C}$ , have been observed for material exposed to room temperature ( $21\text{--}23^\circ\text{C}$ ) ambient atmospheres with dewpoints ranging from  $5^\circ\text{C}$  to saturation, and at atmospheric carbon dioxide vapor pressure, as well as restricted carbon dioxide exposure, for times ranging from one hour to a few hundred hours. Evidence of reaction with not only water vapor, but also with atmospheric carbon dioxide has been obtained. Substantial formation of barium hydroxide octahydrate is noted along with barium carbonate and calcium hydroxide. For materials exposed over extended time periods weight losses approaching 40% are observed indicating the extensive level of reaction which may occur.

## Introduction

In the handling and storage of impregnated dispenser type cathodes it has long been recognized that interaction with certain constituents of the sea level ambient atmosphere was potentially damaging.

The details of the chemistry involved have not been the subject of serious research, and the available information has been purely empirically derived. It is widely believed that hydrolysis of the barium calcium aluminate (BCA) impregnant as a result of exposure to atmospheric water vapor is the critical chemical process.

## Background

The impregnated dispenser-type cathode consists of a porous (about 20% by volume porosity typical) refractory metal (usually tungsten) matrix which is infiltrated with an oxide compound generally referred to as impregnant. The impregnant materials are comprised of barium calcium aluminates, and serve as the source of barium adsorbates, required for activation of the cathode's emitting surface, which are released during operation by complex thermochemical reactions. Such a device is shown schematically in Figure 1 to clarify the physical arrangement of the components of the cathode. Typical tungsten particle size is of the order of five micrometers diameter, and typical pore sizes are one to two micrometers diameter.

The effects of the reaction(s) of the aluminates with atmospheric components are often manifested by "blooming", or the appearance of small amounts of impregnant-derived reaction products on the cathode surface, typically at pore ends, resulting in a hazy appearance. The appearance of material on the cathode surface results from a significant volume expansion of aluminate which originally occupied the near-surface region of the matrix porosity. In the extreme this expansion may result in fracture of the matrix material if aluminate material at significant depth in the matrix is involved.

As a consequence of heating during cathode processing or activation the products of the reaction with atmospheric constituents will undergo decomposition. At least two undesirable results have been attributed to the decomposition reaction(s). The first is that evolving gaseous products may crack the matrix if they are unable to escape the interior through the porosity with sufficient rapidity to avoid internal pressure buildup. This results in the phenomenon known in the industry as "blistering". A second possible result is the formation of complex tungstates or other compounds by reaction with the matrix. This process is most likely begun as a result of rapid evolution of oxygen containing gaseous decomposition products which dissociate to some extent at the local temperature. This will provide sufficient oxygen to locally oxidize the matrix material, rendering it sufficiently reactive to rapidly create the tungstates by reaction with one or more constituent compounds of the impregnant material.

While this constitutes a reasonable qualitative description, the details of the reactions hypothesized, the temperatures at which they occur, the extent of weight gains and losses, the identities of evolving species, and the understanding of potential repercussions in cathode performance have not been quantitatively defined previously.

### Experimental Approach

To date this work has involved investigation of only the  $4\text{BaO} \cdot 1\text{CaO} \cdot 1\text{Al}_2\text{O}_3$  composition. This composition is known from the work of Hann<sup>1</sup> to consist of about 4.5 mole percent barium oxide, 13.0 mole percent calcium oxide, and 82.5 mole percent of the tetrabarium aluminate solid solution compound ( $\text{B}_4\text{A}_{\text{ss}}$ ) with approximate composition,  $\text{Ba}_{3.75}\text{Ca}_{0.25}\text{Al}_2\text{O}_7$ . This corresponds to a composition comprised of about 1.18 weight percent free barium oxide, 1.25 weight percent free calcium oxide, and 97.6 weight percent of the  $\text{B}_4\text{A}_{\text{ss}}$  compound; thus the composition is dominated by the barium calcium aluminate compound.

Materials of the 4:1:1 composition were prepared for this

study by the standard method of calcination in air of barium carbonate, calcium carbonate and aluminum oxide mixtures in the appropriate proportions to yield the desired composition. The composition of this material was verified by x-ray diffraction.

Sample materials were in the form of fine powder which had been deagglomerated subsequent to calcination by light grinding in a mortar and pestle. Two different exposure environments were used. In one the material samples were exposed to water vapor saturated air at near 100% relative humidity at laboratory ambient temperature, usually about 22 to 23°C, in closed containers containing an open vessel of distilled water. This arrangement restricted the extent of exposure to atmospheric carbon dioxide.

A second exposure condition consisted of the laboratory ambient atmosphere, normally about 21 to 24°C with a dewpoint of approximately 15°C (i. e., about 60% RH). This allowed exposure to atmospheric carbon dioxide partial pressure. A range of exposure times were used from one hour up to several hundred hours. Weight gain of the materials was monitored, and found to be gradual for exposure times in excess of twenty-four hours. The majority of weight gain occurred in a matter of a few hours, but the details of weight gain rate are yet to be determined.

After exposure the sample materials were analyzed by x-ray diffraction to identify the reaction products. Further study of the material behavior and makeup was performed by thermogravimetric analysis (TGA). The x-ray diffraction was performed utilizing a Rigaku Geigerflex diffractometer using  $\text{CuK}_\alpha$  radiation and a graphite monochromator. The scan rate was  $2^\circ 2\theta$  per minute with a step size of  $0.02^\circ$ . The thermogravimetric analysis was performed in a Perkin-Elmer TGS-2 with a System 7/4 controller over the temperature range from room temperature to 1000°C with a heating rate of 5°C per minute or in a Seiko TG/DTA320 (simultaneous DTA/TGA) up to 1200°C. All TG/DTA runs were performed in an atmosphere of flowing dry nitrogen at atmospheric pressure.

## Results

The x-ray diffraction results are given in Figure 2. Figure 2(a) depicts the diffraction pattern for the as calcined material. The peaks observed are those of the  $\text{Ba}_{3.75}\text{Ca}_{0.25}\text{Al}_2\text{O}_7$  compound. No extraneous peaks are noted, and peaks for barium oxide and calcium oxide are not observed as a result of their minimal content. Figure 2(b) shows the diffraction pattern for a material exposed to the laboratory ambient environment for about 200 hours, or until reasonable stability was achieved.

Barium hydroxide octahydrate,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ; barium carbonate and calcium hydroxide are unambiguously identified constituents. There are also one or more unidentified phases present. When samples were exposed to water vapor saturated air in a closed vessel, where carbon dioxide exposure was limited to only the gas present in the vessel at the time of sealing, the extent of barium carbonate formation was significantly reduced.

Figure 3 shows the results of TGA over the temperature range from room temperature ( $30^\circ\text{C}$ ) to  $1000^\circ\text{C}$  for a sample exposed primarily to water vapor, i. e., in a closed container as described above. Most notable is the extent of the total weight loss, amounting to about 40% of the initial (hydrated) sample weight.

Figure 4 shows the weight loss behavior of a 4:1:1 sample, after exposure to laboratory ambient for several hundred hours, over the temperature range from 30 to  $1200^\circ\text{C}$ .

In each of the TGA results seven weight loss events have been identified. The initiation temperature ( $T_i$ ), the temperature of the loss rate peak ( $T_p$ ), and the temperature at which each event concludes ( $T_c$ ), along with the percentage of weight lost for each event are listed in Tables IA and IB, respectively.

## Discussion

The first three weight loss events (Event No's. 1, 2 and 3 in Tables IA and B) for each sample are similar to those noted by Habashy and Kolta<sup>2</sup> for a barium hydroxide octahydrate material formed by recrystallization. This decomposition sequence is

interpreted to be comprised of an initial decomposition to the barium hydroxide dihydrate followed by subsequent steps of decomposition to the monohydrate and the anhydrous barium hydroxide. This behavior is differentiated from that of a rehydrated monohydrate.

In Figure 5 TGA results obtained from a commercially obtained sample of barium hydroxide octahydrate are given for reference to the results with the 4:1:1 material. The behavior observed for this material is reminiscent of that reported by Habashy and Kolta for the rehydrated monohydrate. The decomposition of this material is surmised to proceed in two steps, namely the decomposition of the octahydrate to the monohydrate followed by decomposition to the anhydrous barium hydroxide. This behavior has also been reported by Maneva-Petrova and Nikolova.<sup>3</sup>

For the material exposed under conditions limiting the CO<sub>2</sub> exposure the largest single weight loss event is the result of the decomposition of barium hydroxide octahydrate, amounting to about 24% of the sample weight, as noted in Table IA. For this material the event occurs, in three stages, over the temperature range from room temperature to about 160°C.

For the sample exposed to laboratory ambient the overall behavior is very similar. However, the temperature range over which the entire sequence occurs is limited to room temperature up to about 122°C. Similar variations have been noted for individual samples of materials exposed under both conditions, and it should also be noted that the two sets of data presented were obtained on two different TGA units. Direct comparison of temperatures between the two systems may not be appropriate, especially in this very low range of temperature, as a result of differences in thermocouple calibration. For the latter material the extent of the weight loss was much smaller, only about 5% of the sample weight.

Although the behavior of the commercial sample of material was dissimilar to that observed for the exposed 4:1:1, it is felt that the x-ray diffraction evidence and the noted similarity to the behavior reported by Habashy and Kolta are conclusive evidence of

the barium hydroxide octahydrate being one of the products formed by exposure of the impregnant to sea-level ambient atmospheric conditions.

It is important to note that, for both samples, however, the extent of the weight loss associated with the decomposition of the barium hydroxide octahydrate (and/or barium carbonate, as will be discussed subsequently) is much greater than that consistent with formation of the hydrated phase and/or barium carbonate from only the free barium oxide present in the starting composition. It is evident that decomposition of the  $B_4A_{11}$  compound must also take place to yield barium oxide which subsequently forms the octahydrate (and barium carbonate when exposed to  $CO_2$ ). A quantitative estimate of the extent of this reaction has not yet been made.

Figures 6 and 7 provide similar basis for comparisons of the decomposition behaviors of the 4:1:1 material to those of calcium hydroxide and barium carbonate, both of which were identified as constituent phases in the x-ray diffraction analysis. The evidence for decomposition of barium carbonate, Event No. 7 in both samples, is compelling; amounting to about 5.3% in the sample whose exposure to  $CO_2$  was limited, and representing the largest weight loss event, nearly 10%, for the sample exposed to laboratory ambient.

The evidence for calcium hydroxide decomposition occurring in both of the 4:1:1 samples is clear, perhaps at a somewhat lower temperature than observed for the standard compound; but the decomposition of the anhydrous barium hydroxide,  $Ba(OH)_2$ , is reported to occur in the same range. Thus it is likely that Event No. 6 in both samples represents the decomposition of both hydroxides.

Evidence for the decomposition of calcium carbonate was sought by comparison to a standard, but, consistent with the x-ray diffraction data, no indication of its presence was found.

In total, seven significant weight loss events have been recognized for both sample types; however, only five are believed to have been positively identified.



Two weight loss events, Event No's. 4 and 5 for each sample, have not yet been attributed to decomposition of particular phases. There is a similar discrepancy in the temperatures of occurrence of these two events in the two samples to that noted above for the first three events. In the laboratory ambient exposed sample the two events occur over the ranges 148 to 184°C and 205 to 276°C, while in the other sample the temperature ranges are 166 to 200°C and 213 to 235°C. The extent of loss for Event 4 is reasonably comparable in each case, 3.2% and 2.6%, respectively; however, in the case of Event 5, the laboratory ambient exposure results in a loss of 2.7% versus only 0.7% in the other sample. Whether this is indicative of Event No. 5 being related to a carbonate decomposition is not known, but such an argument is plausible. The calcium carbonate decomposition considered would occur at a much higher temperature, however.

Table II provides a synopsis of the identified weight loss events and the equations for the reactions believed to be occurring at each event.

No phases have been identified in the exposed materials which contain the aluminum oxide of the  $B_4A_{12}$  starting compound. A number of hydrated barium aluminate phases are known to exist<sup>4,5</sup> and it is likely that compounds, probably containing calcium in solid solution, related to these account for the unaccounted for peaks in the x-ray diffraction data and the unidentified weight loss events in the TGA results. No documentation of such compounds containing calcium in solid solution has been found in the literature, thus no x-ray data is available to assist in identification.

Efforts have been made to identify the dehydrated products, which result from the decomposition of the hydrated 4:1:1 material, without success. The x-ray diffraction patterns indicate that this material is amorphous or of such poor crystallinity and/or fine crystallite size that peak broadening is overwhelming and no discernible peaks are obtained. It is of interest to speculate at this point, however, that the large amount of the barium hydroxide octahydrate (and barium carbonate) formed will result in a phase

assemblage with much greater barium oxide content than the starting anhydrous 4:1:1 composition. Implications for very high initial evaporation rates from 4:1:1 impregnated cathodes exposed to sea-level ambient atmosphere and subsequently heated are obvious.

### Conclusions

The exposure of 4:1:1 impregnant material to significant partial pressures of water vapor results in the rapid formation of barium hydroxide octahydrate, calcium hydroxide, barium carbonate and other, as yet unidentified products. If the exposure atmosphere contains carbon dioxide there is concomitant conversion of the barium hydroxide octahydrate to barium carbonate. The total weight gain as a result of these reactions can be large, amounting to upwards of 60% of the starting (anhydrous) weight.

The decomposition behavior indicates that the barium hydroxide octahydrate/barium carbonate formation is greater than that expected for hydration of the free barium oxide, which is known to compose only a small percentage of the equilibrium 4:1:1 composition, indicating that decomposition of the  $Ba_{3.75}Ca_{0.25}Al_2O_7$  compound occurs yielding barium oxide which in turn hydrates. Further study of the decomposition process is required to completely identify the decomposition products and their relative levels of occurrence.

## References

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2. Habashy, G. M. and Kolta, G. A., J. Inorg. Nucl. Chem., 34, pp. 57-67 (1972).
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4. Carlson, E. T. et al, Journal of Research of the National Bureau of Standards, 45, (5), pp. 381-398 (1950).
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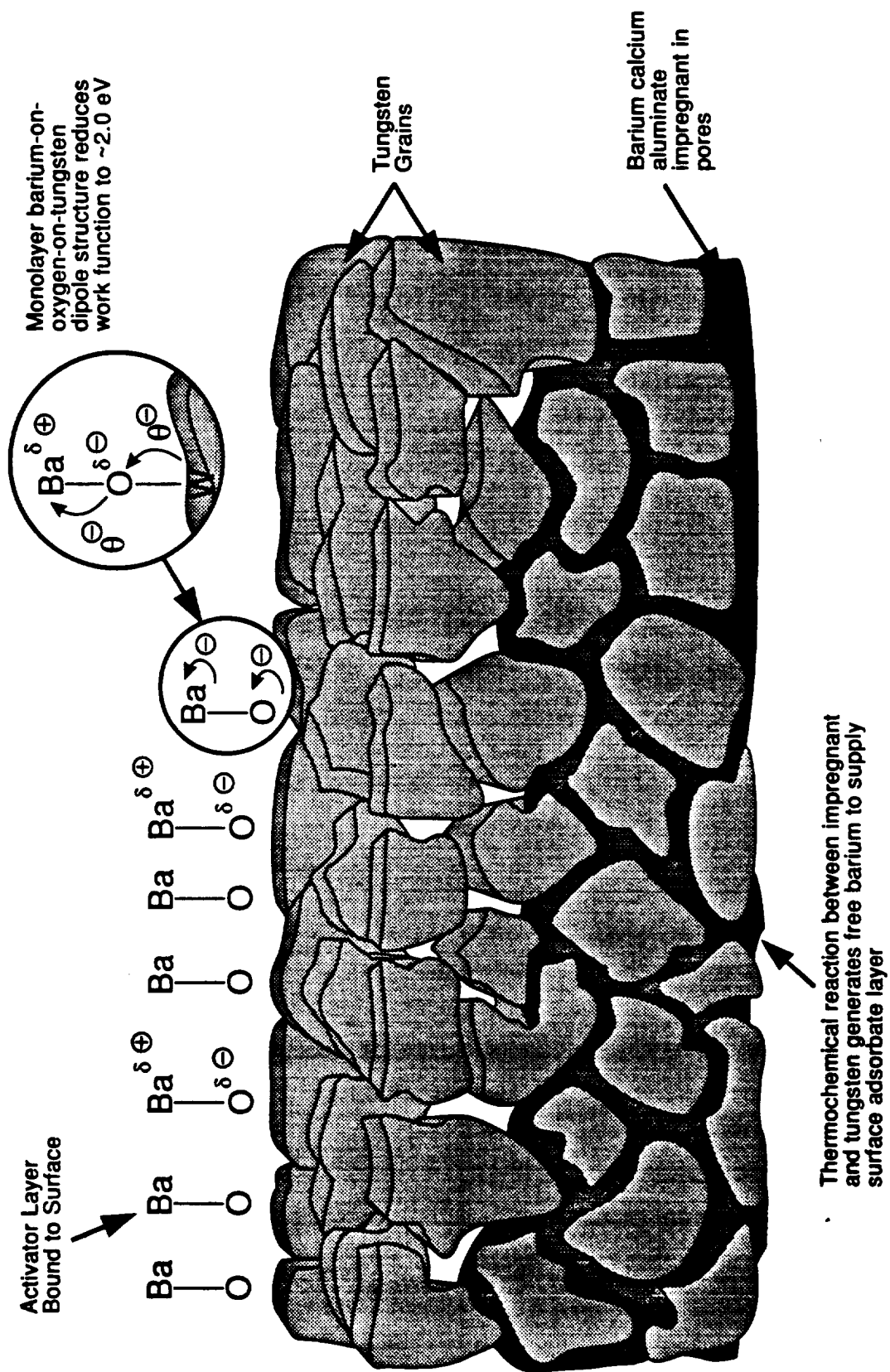


Figure 1 -- Schematic Representation of an Impregnated Dispenser-Type Cathode

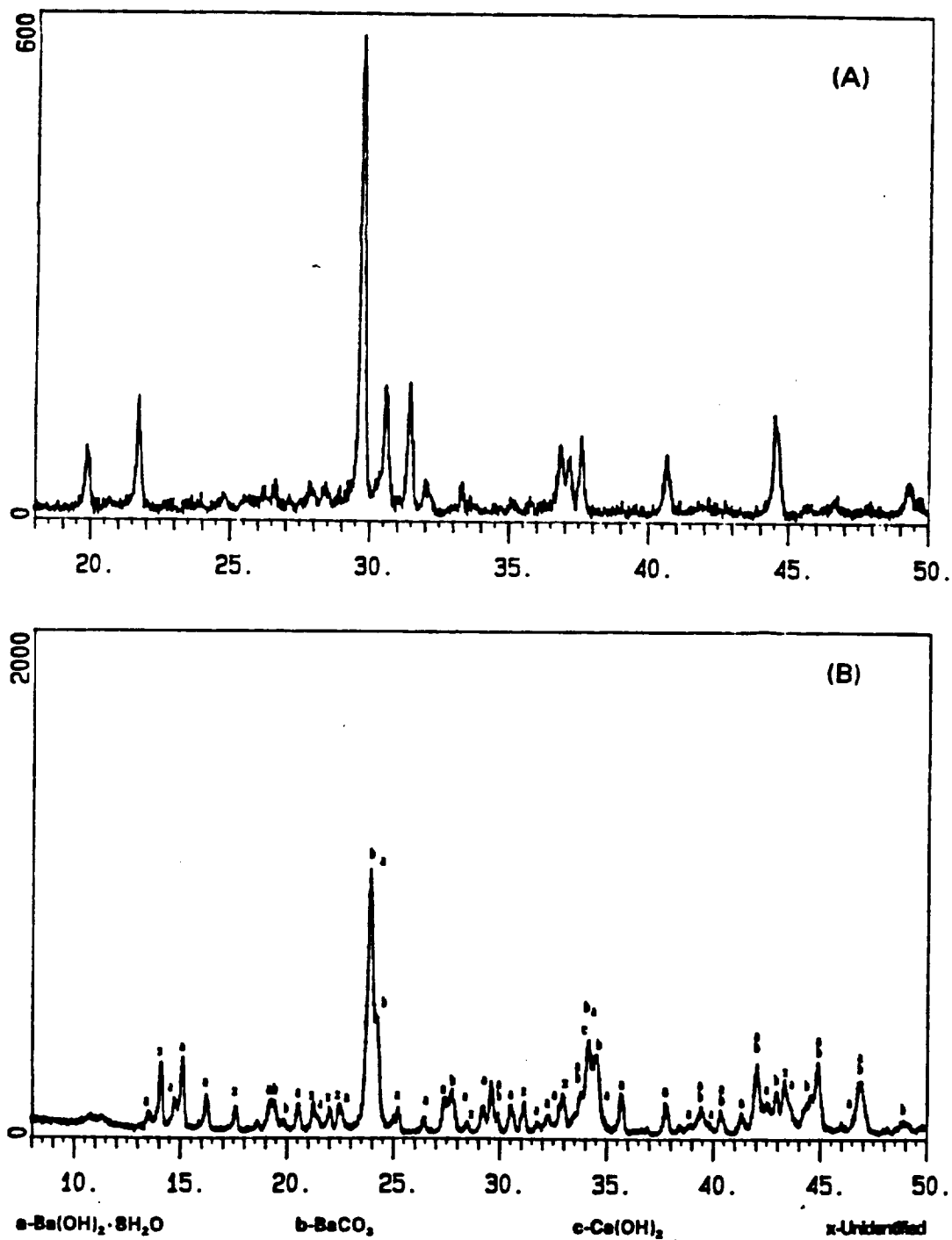


Figure 2 -- X-Ray Diffraction Patterns for (A) As Prepared  $4\text{BaO} \cdot 1\text{CaO} \cdot 1\text{Al}_2\text{O}_3$  and (B)  $4 \cdot 1 \cdot 1$  Exposed to Laboratory Ambient for circa 200 hours

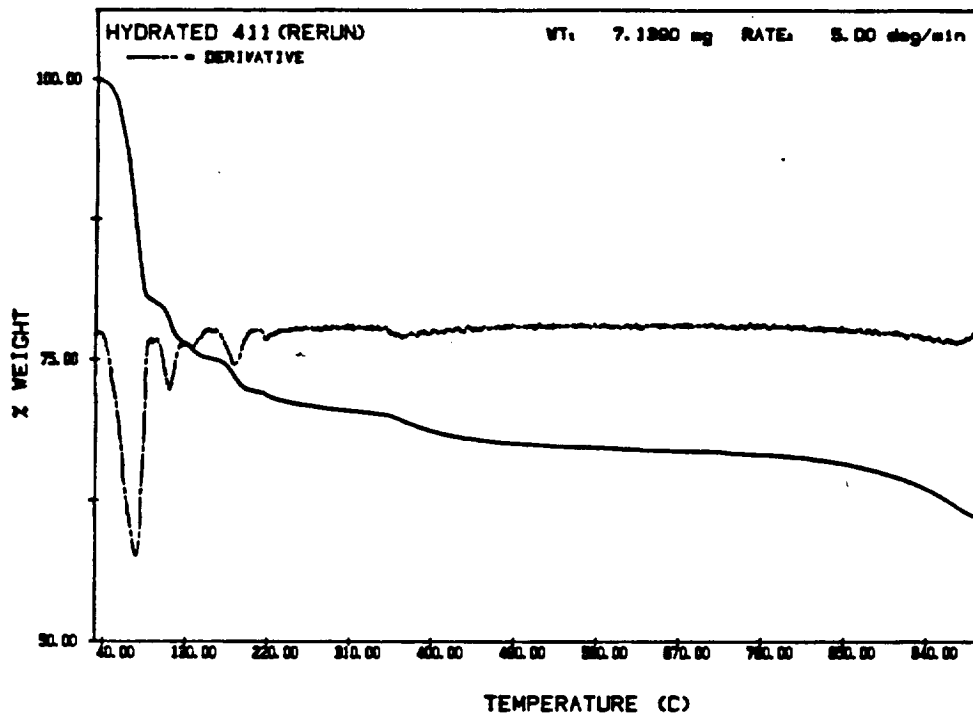


Figure 3 -- Thermogravimetric Analysis Results for 4-1-1 Exposed to Water Vapor with Limited Carbon Dioxide Exposure for circa 200 Hours

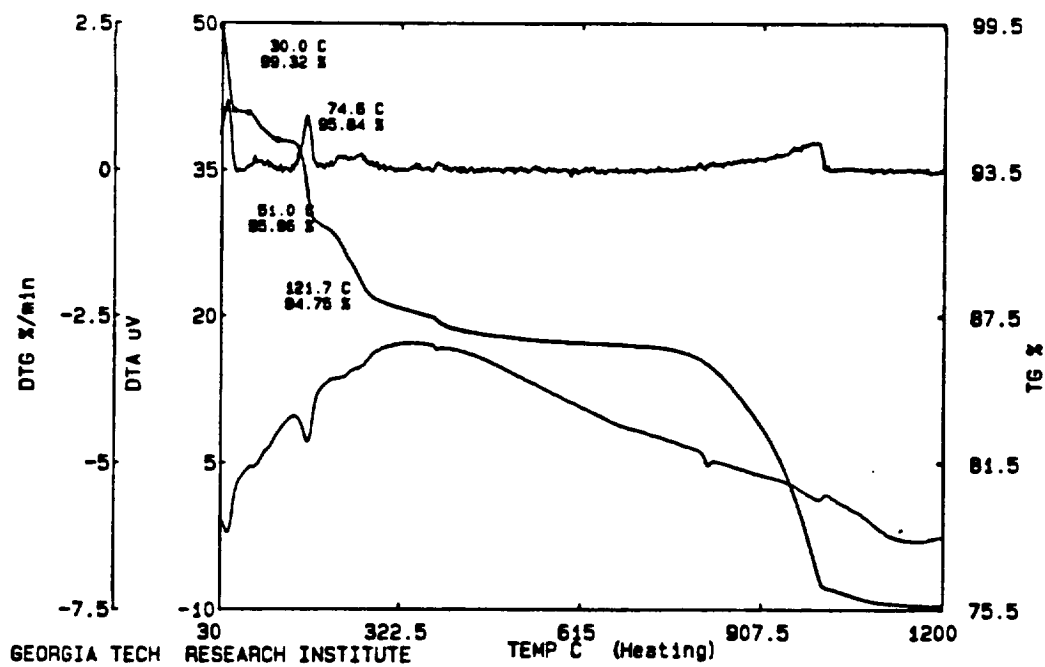


Figure 4 -- Thermogravimetric Analysis Results for 4-1-1 Exposed to Laboratory Ambient for circa 200 Hours

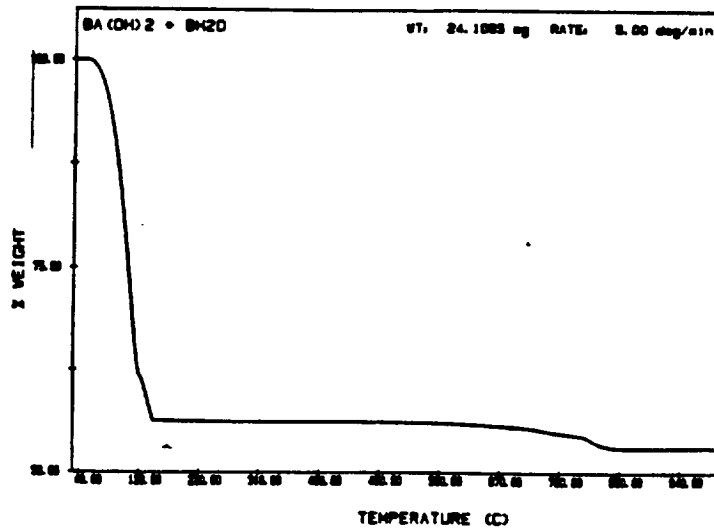


Figure 5 -- Thermogravimetric Analysis Results for Barium Hydroxide Octahydrate  $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$  from J. T. Baker (Catalog No. 1006-01)

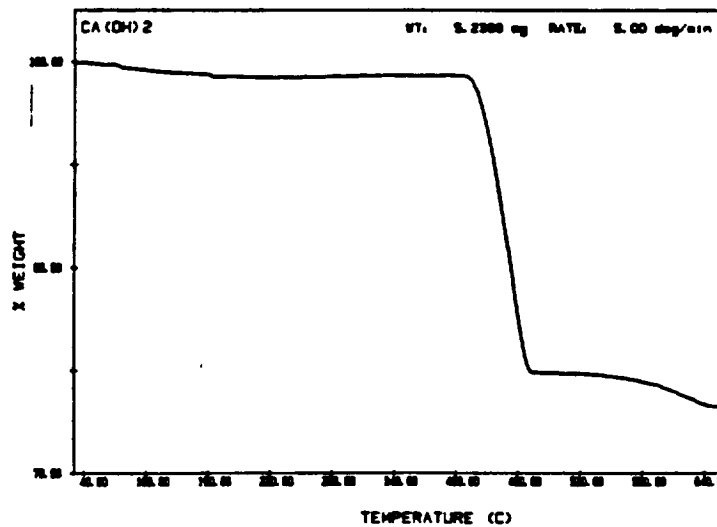


Figure 6 -- Thermogravimetric Analysis Results for Calcium Hydroxide  $[\text{Ca}(\text{OH})_2]$  from J. T. Baker (Catalog No. 1372-01)

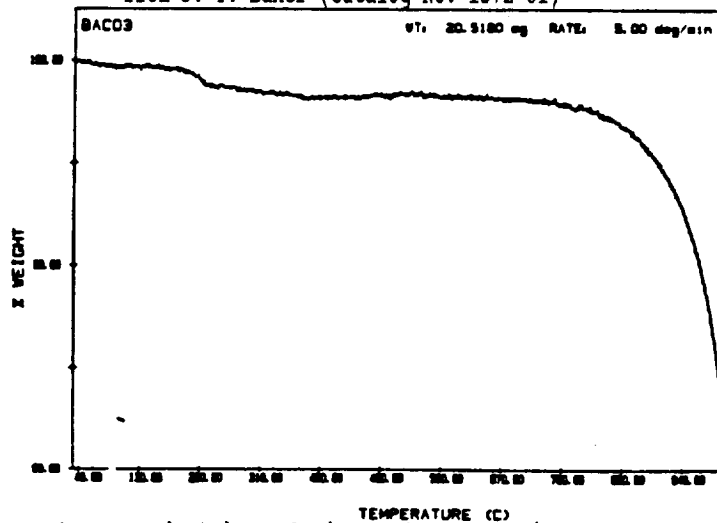


Figure 7 -- Thermogravimetric Analysis Results for Barium Carbonate  $[\text{BaCO}_3]$  from J. T. Baker (Catalog No. 0950-05)

# SUMMARY OF RESULTS FOR THERMOGRAVIMETRIC ANALYSIS

Table IA

EXPOSURE CONDITION -- WATER VAPOR SATURATED, LIMITED CO<sub>2</sub>

<u>Event No.</u>	<u>Temperature, °C</u>			<u>% Wt. Loss</u>
	<u>T<sub>i</sub></u>	<u>T<sub>p</sub></u>	<u>T<sub>c</sub></u>	
1	42	75	88	19.1
2	101	112	122	3.1
3	124	143	159	1.9
4	166	183	200	2.6
5	213	217	235	0.7
6	351	369	439	2.1
7	794	974	1000 <sup>†</sup>	5.3

Table IB

EXPOSURE CONDITION -- LAB AMBIENT, ATMOSPHERIC CO<sub>2</sub>

<u>Event No.</u>	<u>Temperature, °C</u>			<u>% Wt. Loss</u>
	<u>T<sub>i</sub></u>	<u>T<sub>p</sub></u>	<u>T<sub>c</sub></u>	
1	<30	40	51	4.0
2	75	85	96	0.6
3	96	96	122	0.5
4	148	169	184	3.2
5	205	257	276	2.7
6	373	384	428	0.6
7	760	996	1012	9.8



Table II

## DECOMPOSITION REACTION EQUATIONS FOR EACH EVENT

<u>Event No.</u>	<u>Reaction</u>
1	$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 \cdot 2\text{H}_2\text{O} + 6\text{H}_2\text{O}\uparrow$
2	$\text{Ba(OH)}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}\uparrow$
3	$\text{Ba(OH)}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 + \text{H}_2\text{O}\uparrow$
6	$\text{Ba(OH)}_2 \rightarrow \text{BaO} + \text{H}_2\text{O}\uparrow$ $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}\uparrow$
7	$\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2\uparrow$

No reactions identified for Events 4 and 5

